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## The Direct Synthesis of Hydrogen Peroxide from H<sub>2</sub> and O<sub>2</sub> Using Pd-Ni/TiO<sub>2</sub> Catalysts.

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### Summary.

The direct synthesis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) from molecular H<sub>2</sub> and O<sub>2</sub> offers an attractive solution to decentralised production compared to the anthraquinone process. Herein we evaluate the performance of a 0.5%Pd-4.5%Ni/TiO<sub>2</sub> catalyst in batch and flow reactor systems using water as a solvent at ambient temperature which makes synthesising high H<sub>2</sub>O<sub>2</sub> concentrations challenging. Catalyst activity was observed to be stable to prolonged use in multiple batch experiments or in a flow system, with selectivities towards H<sub>2</sub>O<sub>2</sub> of 97% and 85% respectively. This study was carried out in the absence of halide or acid additives that are typically used to inhibit sequential H<sub>2</sub>O<sub>2</sub> degradation reactions showing that this Pd-Ni catalyst has potential to produce H<sub>2</sub>O<sub>2</sub> selectively

### Introduction.

The direct synthesis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) would offer an attractive alternative to the current anthraquinone oxidation (AO) process and potentially allow decentralised production. Accounting for more than 95 % of global H<sub>2</sub>O<sub>2</sub> production the AO process is highly optimised. However there are concerns regarding the requirement for continuous replacement of the anthraquinone as a result of its over-hydrogenation and high energy requirements during the extraction and concentration of the formed H<sub>2</sub>O<sub>2</sub>. Furthermore, the AO process only proves to be economical on a large scale meaning that production has to be centralised. As a result H<sub>2</sub>O<sub>2</sub> is often transported at high concentrations in the presence of acidic stabilisers, used to inhibit decomposition to H<sub>2</sub>O. However, the use of such stabilizing agents often leads to decreased reactor lifetime and increased costs associated with their removal from product streams.

The direct synthesis of H<sub>2</sub>O<sub>2</sub> from molecular H<sub>2</sub> and O<sub>2</sub> would offer an attractive alternative to the AO process, allowing for decentralized H<sub>2</sub>O<sub>2</sub> production. The high activity of Pd-based catalysts for the direct synthesis reaction has been well known since 1914(1) and has received significant attention in the literature.(2-6) However, issues around selectivity have posed a major challenge to suppress H<sub>2</sub>O<sub>2</sub> degradation pathways and can often only be achieved in the presence of acid or halide promoters(7-9). By comparison AuPd catalysts

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have been demonstrated to offer excellent selectivities towards  $\text{H}_2\text{O}_2$  in the absence of stabilizing agents.(10-14) More recently we have reported that it is possible to replace Au with more abundant base-metals such as Sn, Ni, Zn and Co, which through exposure to successive calcination-reduction-calcination heat treatment can demonstrate selectivities towards  $\text{H}_2\text{O}_2$  in excess of 95%. This has been attributed to the encapsulation of ultrasmall Pd-rich nanoparticles, responsible for  $\text{H}_2\text{O}_2$  degradation by a secondary metal oxide.(15)

Subsequently further studies have reported enhanced catalytic performance can be achieved through the alloying of Pd with a range of secondary non- or semi-precious metals such as Ag,(16) Sb,(17) Te,(18) Sn(19), Ni(20) and Zn.(21) Enhancement in selectivity is often attributed to a reduction in the amount of extended Pd ensembles, resulting in a reduction in the rates of O-O bond scission, preventing the formation of  $\text{H}_2\text{O}$  from  $\text{H}_2\text{O}_2$  decomposition or over hydrogenation.

In this work, we focus on the efficacy of our recently reported 4.5%Ni-0.5%Pd/ $\text{TiO}_2$  catalyst.(15) In our previous study we highlighted the excellent selectivity towards  $\text{H}_2\text{O}_2$  that can be achieved with this catalysts under conditions optimized for  $\text{H}_2\text{O}_2$  production. Herein we demonstrate good catalytic performance under conditions less conducive towards  $\text{H}_2\text{O}_2$  synthesis such as ambient reaction temperature and using water only as the reaction solvent in the absence of acid and halides (22). We further investigate the efficacy of the 4.5%Ni-0.5%Pd/ $\text{TiO}_2$  catalyst in a flow regime, with the continual production of  $\text{H}_2\text{O}_2$  highly desirable for industrial application.

## Experimental.

### Catalyst Preparation.

Bimetallic 5% PdNi/ $\text{TiO}_2$  catalysts have been prepared on a wt. % basis by a conventional wet impregnation procedure, based on methodology previously reported in the literature.(15) The procedure to produce 0.5%Pd-4.5%Ni/ $\text{TiO}_2$  (1 g) is outlined as follows. Aqueous solutions of  $\text{Pd}(\text{NO}_3)_2$  (0.833 mL, 6 mg  $\text{mL}^{-1}$ , Johnson Matthey) and  $\text{NiCl}_2$  (5 mL, 9 mg  $\text{mL}^{-1}$ , Sigma Aldrich) were combined with  $\text{H}_2\text{O}$  (HPLC grade), in a 50 mL round bottom flask, so that total volume was fixed to 16 mL. The resulting mixture was heated to 80°C in a thermostatically controlled oil bath with stirring (1000 rpm). Upon reaching 80°C  $\text{TiO}_2$  (0.95 g, Degussa, P25) was added, the resulting slurry was then stirred continuously until a thick paste was formed. The paste was dried (110 °C, 16 h) and the resulting solid material was ground prior to calcination (500 °C, 3 h, 20 °Cmin<sup>-1</sup>, static air). This was followed by reduction (200 °C, 2 h, 20 °C min<sup>-1</sup>, 5 %  $\text{H}_2$ / Ar) and re-calcined (400 °C, 3 h, 20 °Cmin<sup>-1</sup>, static air).

### Direct Synthesis of $\text{H}_2\text{O}_2$ using batch reactor conditions.

$\text{H}_2\text{O}_2$  synthesis was evaluated using a Parr Instruments stainless steel autoclave with a internal volume of 50 mL, equipped with a PTFE liner so that total volume is reduced to 33 mL, and a maximum working pressure of 140 bar. The autoclave liner was charged with catalyst (0.01 g) and solvent (8.5 g  $\text{H}_2\text{O}$ ), then purged three times with 5%  $\text{H}_2$  /  $\text{CO}_2$  (0.7 MPa) before filling with 5 %  $\text{H}_2$  /  $\text{CO}_2$  to a gauge pressure of 29 bar, followed by the addition of 25 %  $\text{O}_2$  /  $\text{CO}_2$  (11 bar). The reaction was conducted at a temperature of 20 °C for 0.5 h with stirring (1200 rpm). The above reaction parameters are based on optimum conditions we have previously used for the synthesis of  $\text{H}_2\text{O}_2$ .(22, 23) The concentration of  $\text{H}_2\text{O}_2$  was determined by titrating aliquots of the final solution after reaction with acidified  $\text{Ce}(\text{SO}_4)_2$  (0.0085 M) in the presence of ferroin indicator. The conversion of  $\text{H}_2$  and selectivity towards  $\text{H}_2\text{O}_2$  were determined using a Varian 3800 GC fitted with TCD and equipped with a Porapak Q column.

$\text{H}_2$  conversion (Equation 1) and  $\text{H}_2\text{O}_2$  selectivity (Equation 2) are defined as follows:

$$\text{H}_2\text{Conversion (\%)} = \frac{\text{mmol}_{\text{H}_2(t(0))} - \text{mmol}_{\text{H}_2(t(1))}}{\text{mmol}_{\text{H}_2(t(0))}} \times 100 \text{ (eq 1)}$$

$$\text{H}_2\text{O}_2 \text{ Selectivity (\%)} = \frac{\text{H}_2\text{O}_2 \text{ detected (mmol)}}{\text{H}_2 \text{ consumed (mmol)}} \times 100 \text{ (eq 2)}$$

### Degradation of H<sub>2</sub>O<sub>2</sub> in a batch reactor.

Catalytic activity towards H<sub>2</sub>O<sub>2</sub> degradation was determined in a similar manner to the direct synthesis activity of a catalyst. The autoclave liner was charged with H<sub>2</sub>O<sub>2</sub> (50 wt. % 0.69 g), H<sub>2</sub>O (7.82 g) and catalyst (0.01 g), with the solvent composition equivalent to a 4 wt. % H<sub>2</sub>O<sub>2</sub> solution. From the solution, two 0.05 g aliquots were removed and titrated with acidified Ce(SO<sub>4</sub>)<sub>2</sub> solution using ferroin as an indicator to determine an accurate concentration of H<sub>2</sub>O<sub>2</sub> at the start of the reaction. The autoclave was pressurised with 2.9 MPa 5 % H<sub>2</sub> / CO<sub>2</sub> (gauge pressure). The reaction was conducted at a temperature of 20 °C, for 0.5 h with stirring (1200 rpm). After the reaction was complete the catalyst was removed from the reaction mixture and two 0.05 g aliquots were titrated against the acidified Ce(SO<sub>4</sub>)<sub>2</sub> solution using ferroin as an indicator. Catalytic activity towards H<sub>2</sub>O<sub>2</sub> degradation is reported herein as % degradation and accounts for hydrogenation and decomposition pathways. The reactor temperature was controlled using a HAAKE K50 bath/circulator using an appropriate coolant.

### Direct Synthesis of H<sub>2</sub>O<sub>2</sub> in a flow reactor.

A continuous, fixed-bed reactor was constructed for the direct synthesis of H<sub>2</sub>O<sub>2</sub> using Swagelok fittings with an internal diameter of 1/4 inch. Gas flows of 5 % H<sub>2</sub>/CO<sub>2</sub> and 25 % O<sub>2</sub>/CO<sub>2</sub> were controlled using Brooks mass flow controllers with the pressure maintained and controlled using a back-pressure regulator at the end of the system. Pressure relief valves were included at various points throughout the system to release pressure in the case of a blockage. Water (HPLC grade) free from acid or halide additives was used as the reaction medium and pumped through the system using an Agilent 1260 series isocratic HPLC pump, a gas liquid separator (GLS) and one-way valves were placed after the MFCs to prevent any liquid from entering the MFCs during the reaction. Liquid was collected downstream before the back-pressure regulator by emptying a 150 mL GLS fitted with a valve which acted as a sample collection vessel. A schematic of the reactor is shown in Figure S.1.

A typical H<sub>2</sub>O<sub>2</sub> synthesis reaction was carried out using between 0.05 and 0.25 g of catalyst, which had been pressed into a disk and sieved to a particle size of 425–600 µm. The sample was supported at the bottom of the catalyst bed in the reactor tube by glass wool. The catalyst was contained within a 10 cm stainless steel tube with an internal diameter of 1/4 inch. The reactor system was then pressurized, typically to 30 bar, with a 1:1 mixture of H<sub>2</sub> and O<sub>2</sub> from the respective CO<sub>2</sub> diluted cylinders. The reactor temperature was controlled using a water bath at 20 °C. When the reaction pressure and gas flows stabilised the solvent flow (typically, 0.25 - 5.0 mLmin<sup>-1</sup>) was introduced into the system. Both gas and liquid flowed concurrently through the catalyst bed from top to bottom. Liquid samples were taken from the sample bomb every 10 min, and the concentration of H<sub>2</sub>O<sub>2</sub> was determined by titration against an acidified dilute Ce(SO<sub>4</sub>)<sub>2</sub> solution using ferroin as an indicator. During the study, the amount of H<sub>2</sub>O<sub>2</sub> was quoted as the concentration formed in the reaction solution in units of parts per million (ppm). Selectivity towards H<sub>2</sub>O<sub>2</sub> synthesis was determined via GC analysis, as discussed above. Evaluation of the activity of the uncharged (no catalyst) reactor towards H<sub>2</sub>O<sub>2</sub> degradation and synthesis is found to be zero in both respects.

### Characterisation.

Metal leaching from supported catalyst was quantified using microwave plasma atomic emission spectroscopy (MP-AES) via analysis of filtered post reaction solutions, using an Agilent 4100 MP-AES. The

concentration responses of Ni and Pd were calibrated using commercial reference standards (Agilent); in all cases  $r^2 > 0.999$ .

## Results and Discussion.

Our initial work focused on the evaluation of 5%PdNi/TiO<sub>2</sub> catalysts with varied Pd: Ni ratios for the direct synthesis and subsequent degradation of H<sub>2</sub>O<sub>2</sub>. We used water as the solvent in the absence of halide or acid as promoters and ambient temperature both of which are not favourable conditions to suppress H<sub>2</sub>O<sub>2</sub> degradation (Figure 1). (22, 23) A correlation between total Pd content and catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis was observed, with observed H<sub>2</sub>O<sub>2</sub> increasing to a maximum of 312 ppm for the 0.75%Pd-4.25%Ni/TiO<sub>2</sub> catalyst before plateauing as the composition was varied to 1%Pd-4%Ni/TiO<sub>2</sub> after 30 min of reaction. Interestingly no activity towards H<sub>2</sub>O<sub>2</sub> degradation, via decomposition or hydrogenation pathways, was observed for the 0.75%Pd-4.25%Ni/TiO<sub>2</sub> catalyst or those materials with lower Pd loadings, despite their ability to produce H<sub>2</sub>O<sub>2</sub>. Increasing Pd content beyond 15 % of total metal loading does not result in further rise in H<sub>2</sub>O<sub>2</sub> concentration, whereas we observe the development of catalytic activity towards H<sub>2</sub>O<sub>2</sub> degradation (6 %) for the 1%Pd-4%Ni/TiO<sub>2</sub> catalyst.

By comparison we have recently reported (23) that the well-studied 2.5%Au-2.5%Pd/TiO<sub>2</sub> catalyst (24, 25) prepared via a conventional wet-impregnation methodology offers significantly greater rates of H<sub>2</sub>O<sub>2</sub> degradation (25 %), under identical reaction conditions indicating the beneficial effects of alloying Pd with Ni. However, despite the significantly greater activity of the supported AuPd catalyst towards H<sub>2</sub>O<sub>2</sub> degradation the concentration of H<sub>2</sub>O<sub>2</sub> generated (476 ppm)(23) is only slightly greater than that observed for the 0.75%Pd-4.25%Ni/TiO<sub>2</sub> catalyst.

With the requirement for Ni to be present in order to inhibit H<sub>2</sub>O<sub>2</sub> degradation pathways clear (Table S.1), we next evaluated the efficacy of the 0.5%Pd-4.5%Ni/TiO<sub>2</sub> catalyst over multiple sequential H<sub>2</sub>O<sub>2</sub> synthesis tests under batch conditions (Figure 2). After carrying out five consecutive reactions the H<sub>2</sub>O<sub>2</sub> concentration increased in a linear manner to a value of 552 ppm, with no loss in H<sub>2</sub>O<sub>2</sub> selectivity (97 %) over sequential synthesis reactions. Both findings imply that there is no subsequent decomposition or hydrogenation of the H<sub>2</sub>O<sub>2</sub> which is synthesised and un-stabilised in comparison to commercial samples. The high selectivity of the 0.5%Pd-4.5%Ni/TiO<sub>2</sub> catalyst is particularly noteworthy given the relatively unfavourable conditions utilised in this study, namely the use of ambient temperatures and a water only reaction medium.

Typically the evaluation of catalytic performance towards H<sub>2</sub>O<sub>2</sub> synthesis has focussed on the use of high pressure, batch reactors.(26, 27) However, the use of such reactors inherently results in high contact times between the catalyst and synthesised H<sub>2</sub>O<sub>2</sub>, often leading to increased degradation via hydrogenation and decomposition pathways. Alternatively a range of membrane,(28, 29) fixed bed,(30) trickle bed(31-33) and microreactors(34, 35) have been utilised in the direct synthesis of H<sub>2</sub>O<sub>2</sub>. Indeed we have previously reported the efficacy of a 0.5%Au-0.5%Pd/TiO<sub>2</sub> catalyst, towards H<sub>2</sub>O<sub>2</sub> synthesis using a fixed bed reactor, with selectivities of 80 % reached when using optimised reaction conditions.(36) However, it should be noted that when using reaction conditions similar to those used within this work (water only as solvent and ambient temperature) the 0.5%Au-0.5%Pd/TiO<sub>2</sub> catalyst only displayed a selectivity towards H<sub>2</sub>O<sub>2</sub> of approximately 20 %, with a H<sub>2</sub>O<sub>2</sub> concentration of 190 ppm produced. With the commercial production of H<sub>2</sub>O<sub>2</sub> in a continuous mode likely to be favoured, due to minimisation of H<sub>2</sub>O<sub>2</sub> degradation we next investigated the role of key reaction conditions on the formation of H<sub>2</sub>O<sub>2</sub> over the 0.5%Pd-4.5%Ni/TiO<sub>2</sub> catalyst in a fixed bed flow reactor. The effect of varying catalyst mass from 0.05 to 0.25 g was first investigated (Figure 3), with H<sub>2</sub>O<sub>2</sub> concentration increasing in a linear manner with catalyst content up to a catalyst mass of 0.1 g, beyond which H<sub>2</sub>O<sub>2</sub> concentration continues to increase but non-linearly. This in part may be related to a slight rise in activity towards the degradation of H<sub>2</sub>O<sub>2</sub>, as indicated by the marginal decrease in H<sub>2</sub>O<sub>2</sub> selectivity at

increased catalyst mass. Which in turn results from increased contact time between reactant gases and the catalyst. Indeed, the relationship between  $\text{H}_2\text{O}_2$  degradation activity and  $\text{H}_2\text{O}_2$  concentration is well known.<sup>(15)</sup> However, it is more likely, given the relatively high flow rates used within this study that the plateau observed in  $\text{H}_2\text{O}_2$  concentration can be related to limitations associated with reactant gas diffusion to the catalyst. It should be noted that regardless of catalyst mass, selectivity towards  $\text{H}_2\text{O}_2$  remains high, exceeding 85 %.

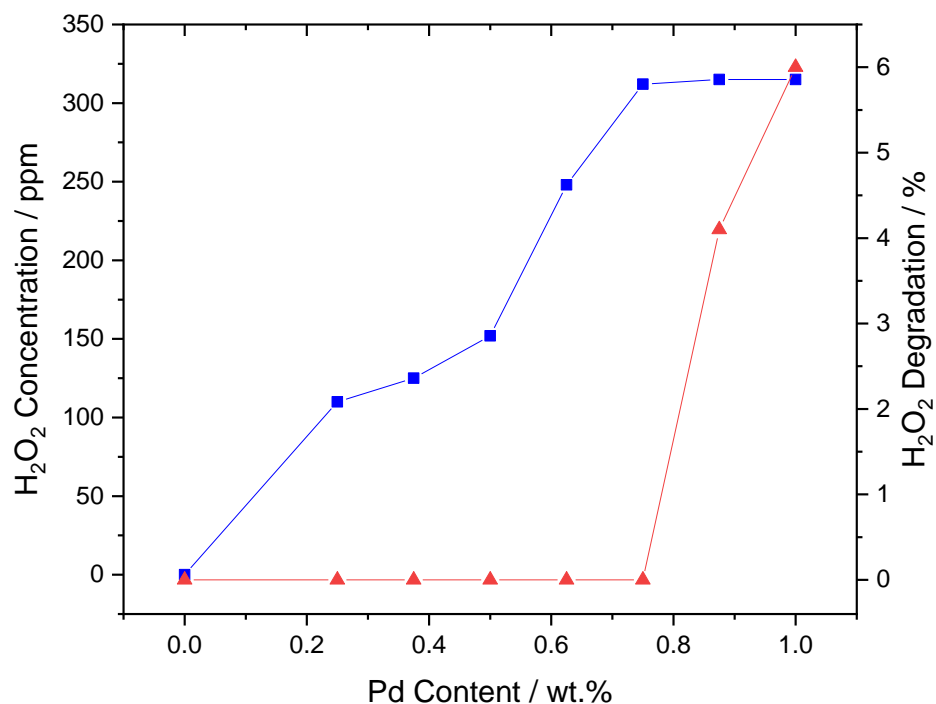
The effect of total reaction pressure was next investigated (Figure 4), while maintaining all other reaction conditions. As expected, an enhancement in  $\text{H}_2\text{O}_2$  concentration was observed with increasing pressure. These results show that pressure had no effect on catalytic selectivity, which remains constant at 85 %. This is in keeping with our previous observations into supported AuPd nanoparticles, under both flow<sup>(36)</sup> and batch<sup>(25)</sup> regimes, where both  $\text{H}_2\text{O}_2$  synthesis and degradation pathways increase proportionally with pressure.

The effect of solvent flow rate was next investigated while maintaining all other reaction conditions (Figure 5). Perhaps unsurprisingly, due to effects of dilution, we observe a decrease in  $\text{H}_2\text{O}_2$  concentration with increasing flow rate. However, calculation of the moles of  $\text{H}_2\text{O}_2$  produced revealed that this metric increased with solvent flow, with a maximum (0.004 mmol) observed at 3 mLmin<sup>-1</sup> solvent flow. Increasing flow rate beyond 3 mLmin<sup>-1</sup> resulted in no further increase in  $\text{H}_2\text{O}_2$  concentration. This is ascribed to mass transfer limitations, where greater solvent flow rates and shorter residence times inhibit diffusion of reagent gases to catalytically active sites.

Finally with the requirement to re-use a catalyst successfully at the heart of green chemistry and the activity of homogeneous species towards  $\text{H}_2\text{O}_2$  synthesis well known,<sup>(37)</sup> we next investigated catalytic activity of the 0.5%Pd-4.5%Ni/TiO<sub>2</sub> catalyst towards  $\text{H}_2\text{O}_2$  synthesis for extended periods of time, under flow conditions (Figure 6). Over 10 h onstream, we observe no loss in either activity, with 80 ppm  $\text{H}_2\text{O}_2$  produced consistently, or selectivity towards  $\text{H}_2\text{O}_2$ , indicative of the high stability of the catalyst. Furthermore, analysis of the post reaction effluent via MP-AES (Table S.2) reveals no leaching of either Pd or Ni from the catalyst surface. It should be noted that comparable concentrations of  $\text{H}_2\text{O}_2$  to that produced over the 0.5%Pd-4.5%Ni/TiO<sub>2</sub> catalyst have previously been reported to offer excellent biocidal activity, with Ronen et al.<sup>(38)</sup> reporting the high efficacy of preformed  $\text{H}_2\text{O}_2$  in the remediation of greywater.

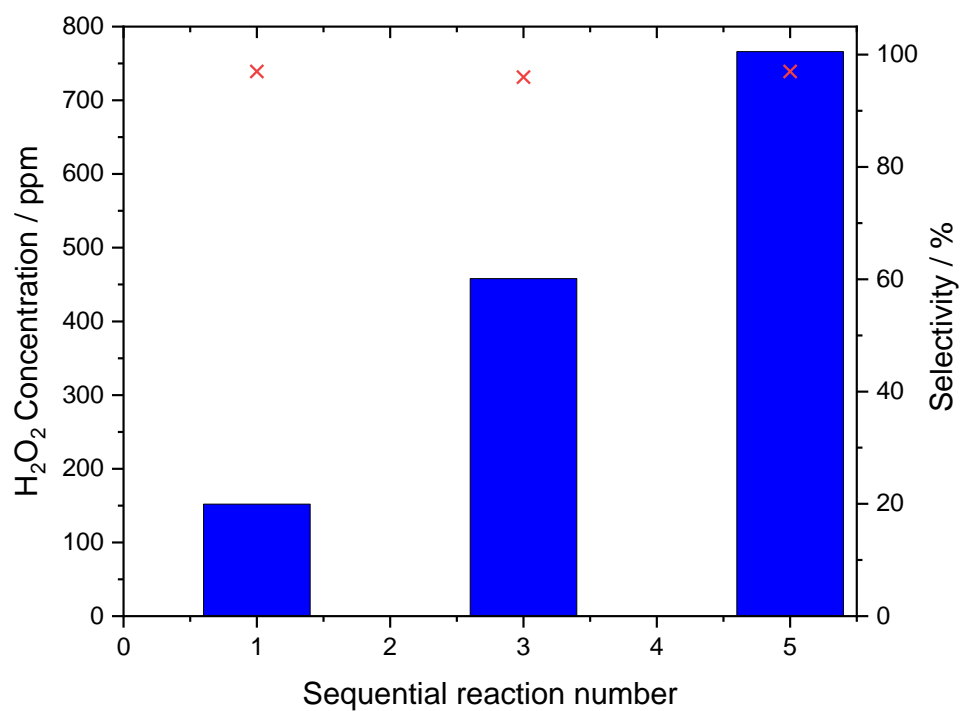
## Conclusion.

With a focus on reaction conditions considered unfavourable to  $\text{H}_2\text{O}_2$  formation we have evaluated the efficacy of supported PdNi catalysts exposed to a successive calcination-reduction-calcination heat treatment towards the direct synthesis of  $\text{H}_2\text{O}_2$ . Catalytic activity in both a stirred autoclave reactor and using flow conditions is found to be stable, with a selectivity towards  $\text{H}_2\text{O}_2$  exceeding 95 and 85 % in batch and flow regimes respectively. We consider that these catalysts represent a promising basis for further exploration for the direct synthesis of  $\text{H}_2\text{O}_2$  under realistic industrial conditions.



**Figure 1.** Catalytic activity of 5%PdNi/TiO<sub>2</sub> toward H<sub>2</sub>O<sub>2</sub> synthesis (squares) and its subsequent degradation (triangles) as a function of Pd content, under batch conditions.

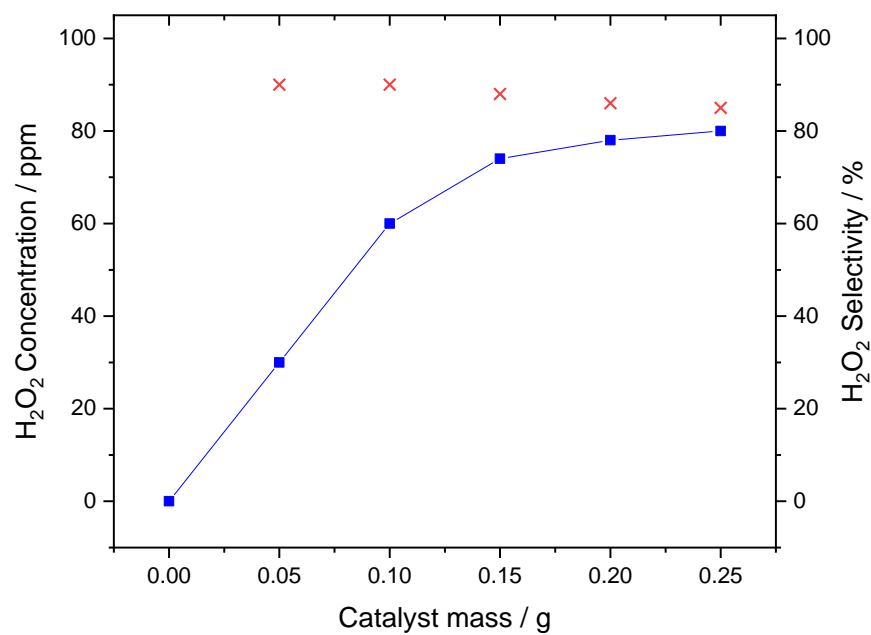
H<sub>2</sub>O<sub>2</sub> direct synthesis reaction conditions: catalyst (0.01 g), H<sub>2</sub>O (8.5 g), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 25% O<sub>2</sub>/CO<sub>2</sub> (160 psi), 0.5 h, 20 °C, 1200 rpm. H<sub>2</sub>O<sub>2</sub> degradation reaction conditions: catalyst (0.01 g), H<sub>2</sub>O<sub>2</sub> (50 wt. %, 0.68 g), H<sub>2</sub>O (7.82 g), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 0.5 h, 20 °C, 1200 rpm.



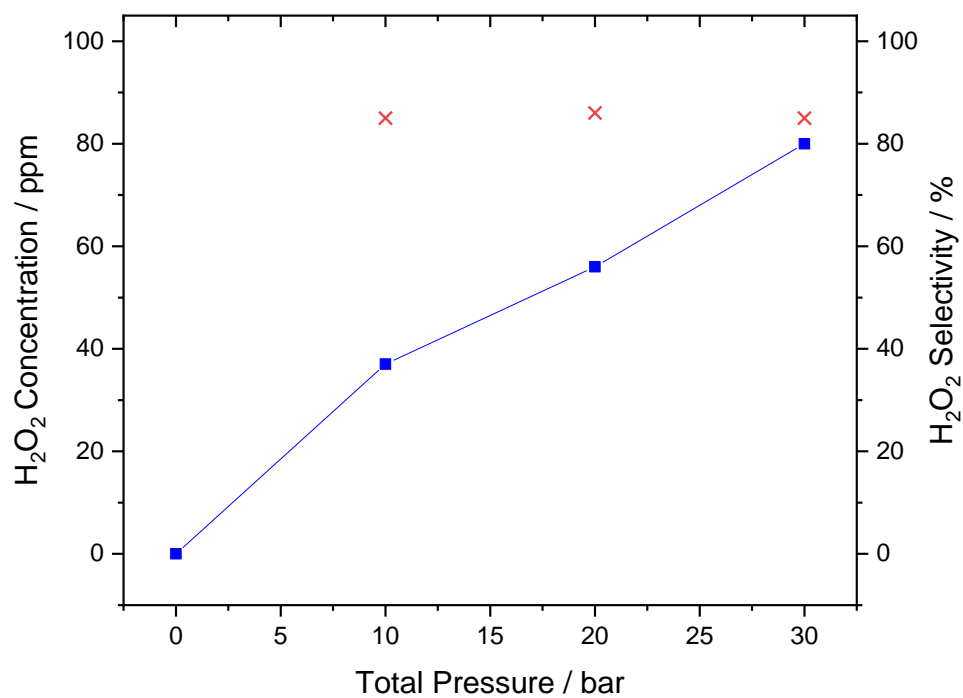
**Figure 2.** Sequential H<sub>2</sub>O<sub>2</sub> synthesis reactions over the 0.5%Pd-4.5%Ni/TiO<sub>2</sub> catalyst, under batch conditions. H<sub>2</sub>O<sub>2</sub> concentration (bar), selectivity towards H<sub>2</sub>O<sub>2</sub> (cross).

H<sub>2</sub>O<sub>2</sub> direct synthesis reaction conditions: catalyst (0.01 g), H<sub>2</sub>O (8.5 g), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 25% O<sub>2</sub>/CO<sub>2</sub> (160 psi), 0.5 h, 20 °C, 1200 rpm.





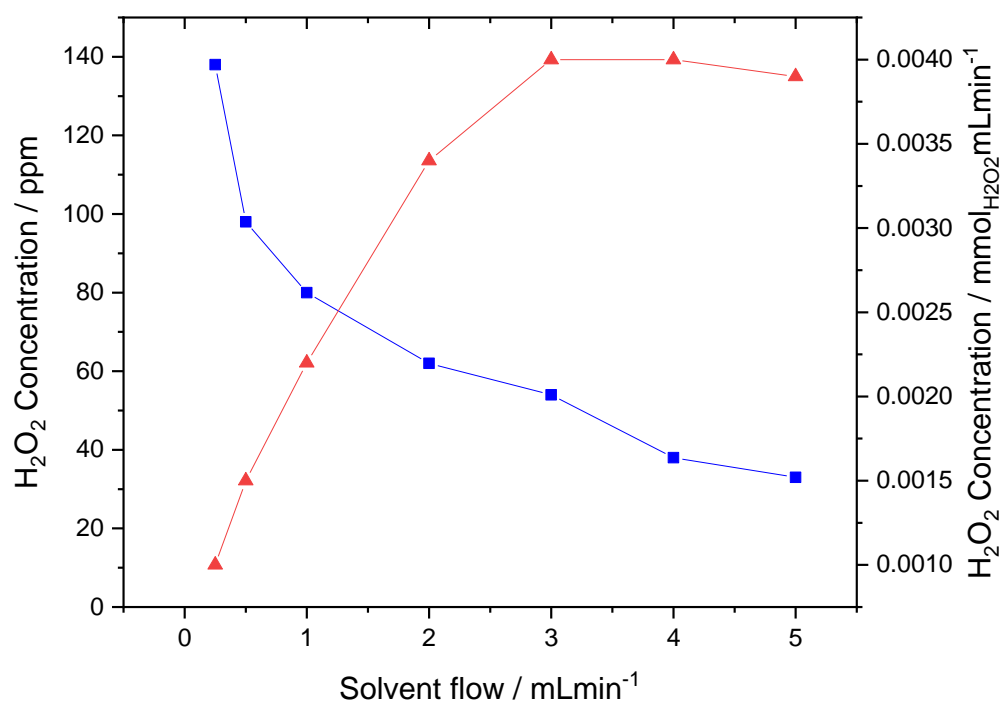
**Figure 3.** Effect of catalyst mass on catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis, under flow conditions. H<sub>2</sub>O<sub>2</sub> concentration (squares), selectivity towards H<sub>2</sub>O<sub>2</sub> (cross).  
Reaction conditions: 20 °C, H<sub>2</sub>O liquid flow rate, 1 mLmin<sup>-1</sup>, 30 bar total pressure, 5% H<sub>2</sub>/CO<sub>2</sub> (175 mLmin<sup>-1</sup>), 25% O<sub>2</sub>/CO<sub>2</sub> (35 mL min<sup>-1</sup>).



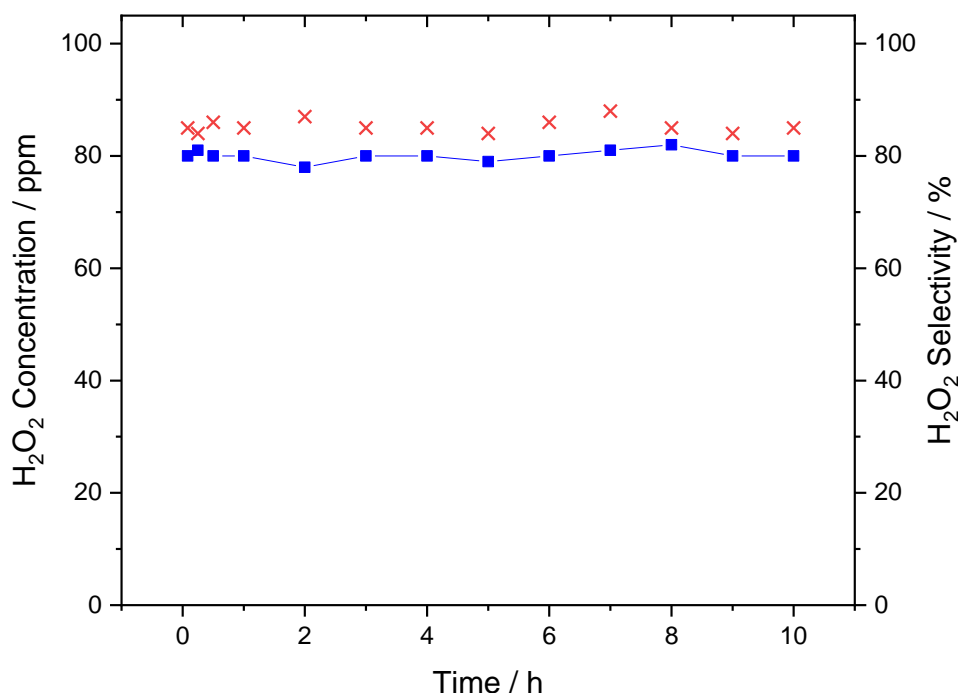
**Figure 4.** Effect of pressure on catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis, under flow conditions.

H<sub>2</sub>O<sub>2</sub> concentration (squares), selectivity towards H<sub>2</sub>O<sub>2</sub> (cross).

Reaction conditions: 20 °C, catalyst mass (0.25 g) H<sub>2</sub>O liquid flow rate, 1 mLmin<sup>-1</sup>, 5% H<sub>2</sub>/CO<sub>2</sub> (175 mLmin<sup>-1</sup>), 25% O<sub>2</sub>/CO<sub>2</sub> (35 mLmin<sup>-1</sup>).



**Figure 5.** Effect of solvent flow rate on catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis, under flow conditions. H<sub>2</sub>O<sub>2</sub> concentration as ppm (squares), H<sub>2</sub>O<sub>2</sub> concentration as mmol<sub>H<sub>2</sub>O<sub>2</sub></sub>mLmin<sup>-1</sup> (triangles). Reaction conditions: 20 °C, catalyst mass (0.25 g) H<sub>2</sub>O, 30 bar total pressure, 5% H<sub>2</sub>/CO<sub>2</sub> (175 mLmin<sup>-1</sup>), 25% O<sub>2</sub>/CO<sub>2</sub> (35 mLmin<sup>-1</sup>).



**Figure 6.** Catalytic activity of the 0.5%Pd-4.5%Ni/TiO<sub>2</sub> catalyst over 10 h onstream. H<sub>2</sub>O<sub>2</sub> concentration (squares), selectivity towards H<sub>2</sub>O<sub>2</sub> (cross).

Reaction conditions: 20 °C, catalyst mass (0.25 g) H<sub>2</sub>O liquid flow rate, 1 mLmin<sup>-1</sup>, 30 bar total pressure, 5%H<sub>2</sub>/CO<sub>2</sub> (175 mLmin<sup>-1</sup>), 25% O<sub>2</sub>/CO<sub>2</sub> (35 mLmin<sup>-1</sup>).

## Additional Information

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### Data Accessibility

Readers should contact LewisR27@Cardiff.ac.uk

### Competing Interests

The authors declare no competing interests.

### Authors' Contributions

All authors provided substantial contributions to the conception and design, or acquisition of data, or analysis and interpretation of data, drafting the article or revising it critically for important intellectual content and final approval of the version to be published.

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